EXPERIMENTAL
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Conductivity Water

Conductivity water was prepared by the following method: Tap water was distilled first with alkaline potassium permanganate and then redistilled with sulfuric acid (Merck) from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel. The conductivity water thus prepared was utilized for the preparation of all the solutions used in the kinetic determinations.

Sulfuric Acid

E. Merck sample was used after a check of its physical constants.

Acetic Acid

Acetic acid (E. Merck) was refluxed for 3 hours with chromic oxide, with the addition of a quantity of acetic anhydride corresponding to the water content of the acetic acid. The solids that separated out were filtered off, and the acid was distilled from an all-glass apparatus. Large head and tail fractions were rejected and the fraction distilling at 116 °C was collected.

Quinolinium Dichromate (QDC), \( (C_9H_7N^+H)_2Cr_2O_7^2- \)

To a stirred solution of \( \text{CrO}_3 \) (100 g) in water (100 ml) cooled in ice, quinoline (86 ml) was added in small proportions. The solution was diluted with acetone (400 ml), cooled to −20 °C, and the orange solid which separated out was filtered,
washed with acetone, dried in vacuo and recrystallized from water (m.p. 160°C). The purity of the compound was further checked by spectral analysis. Infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730 cm\(^{-1}\), characteristic of the dichromate ion.

**Substrates**

Acetaldehyde (S.d. Fine Chem. Ltd.), propionaldehyde, butyraldehyde, valeraldehyde, isovaleraldehyde (Fluka) and isobutyraldehyde (E. Merck) were used after distillation, and their purity was checked from physical constants.

The long chain aliphatic aldehydes (caproaldehyde, heptaldehyde, caprylaldehyde, pelargonaldehyde and caprinaldehyde) obtained from Aldrich, were all distilled before use, and their purity was checked from physical constants.

Glutaraldehyde (S.d. Fine Chem. Ltd.) and glyoxal (S.D's) were distilled and used after checking their physical constants.

2-Furaldehyde (S.d. Fine Chem. Ltd.), 5-methyl-2-furaldehyde, 2-thiophencarbaldehyde, 2-pyridinecarbaldehyde, and 3-pyridinecarbaldehyde (Aldrich), were all distilled before use and their purity was further checked from physical constants. 5-bromo-2-furaldehyde and 2-pyrrololecarbaldehyde (Aldrich) were used after recrystallization and their purity was checked from physical constants.

Acrylaldehyde, methacrylaldehyde (Aldrich) and crotonaldehyde, cinnamaldehyde (Merck-Schuchardt) were used after distillation and their purity was checked from
physical constants. The boiling points and melting points of the substrates used are summarized in Table 1.
Table 1: Boiling Points / Melting Points of Substrates (1)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Boiling points or Melting points (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>20</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>49</td>
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<tr>
<td>Butyaldehyde</td>
<td>75</td>
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<td>Valeraldehyde</td>
<td>104</td>
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<td>Caproaldehyde</td>
<td>131</td>
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<td>Heptaldehyde</td>
<td>155</td>
</tr>
<tr>
<td>Caprylicaldehyde</td>
<td>170</td>
</tr>
<tr>
<td>Pelargonaldehyde</td>
<td>190</td>
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<tr>
<td>Caprinaldehyde</td>
<td>208</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>92</td>
</tr>
<tr>
<td>Isobutyaldehyde</td>
<td>64</td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>101</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>50</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>162</td>
</tr>
<tr>
<td>5-Methyl-2-furaldehyde</td>
<td>187</td>
</tr>
<tr>
<td>5-Bromo-2-furaldehyde</td>
<td>82-84 (m.p)</td>
</tr>
<tr>
<td>2-Pyrrolocarbaldehyde</td>
<td>43-45 (m.p)</td>
</tr>
<tr>
<td>2-Thiophenecarbaldehyde</td>
<td>198</td>
</tr>
<tr>
<td>2-Pyridinecarbaldehyde</td>
<td>181</td>
</tr>
<tr>
<td>3-Pyridinecarbaldehyde</td>
<td>95-97</td>
</tr>
<tr>
<td>Acrylaldehyde</td>
<td>52</td>
</tr>
<tr>
<td>Methacrylaldehyde</td>
<td>73</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>102</td>
</tr>
<tr>
<td>Cinnamaldehyde</td>
<td>252</td>
</tr>
</tbody>
</table>
Acrylonitrile

The monomer (BDH) was washed with 5% sodium hydroxide solution to remove the inhibitor (hydroquinone), and then with 3% orthophosphoric acid to remove any basic impurities. It was then washed with water, dried over anhydrous calcium chloride, and distilled under reduced pressure in an atmosphere of nitrogen. The middle fraction was collected (b.p. 77°C) and used.

Other Reagents

All other reagents used were of AnalaR grade, and were purified before use, and their boiling points / melting points were checked, and found to agree with those given in the literature.

Instruments

(a) FT-IR spectrophotometer: All IR spectra were recorded on FT-IR (DA-8, Bomen) spectrophotometer.

(b) FT-NMR spectrometer: NMR spectra were recorded on FT-NMR (300 MHz, Bruker) spectrometer.

(c) UV-VIS spectrophotometer: For absorption measurements, the spectrophotometer used was Beckman DU 650.

The DU 650 spectrophotometer was a single beam spectrophotometer having a wavelength range from 190 nm to 1100 nm. In order to ensure maximum sensitivity of the instrument, and to minimize
the errors in the measurements of absorbance due to fluctuations in voltage, the spectrophotometer was connected to the mains through an external voltage stabilizer. This was in addition to the in-built voltage stabilizer within the instrument itself. The light source was a 15 watt tungsten lamp operated by a regulated power supply. The spectrophotometer was equipped with the computer device attachment which permitted the recording of the absorbance of unreacted Cr(VI) as a function of time at 440nm (maximum absorption of Cr(VI)). The instrument was equipped with a thermostat compartment of 1 cm cell, the temperature of which was constant to 0.1°C. The compartment was connected to a thermostat for regulating the water circulation at the desired temperature. The spectrophotometer was provided with a parallel output from a Dot Matrix Printer.

A blank reading for the instrument was taken on a cuvette filled with solvent (substrate) before the analysis began. The solvent was at the same temperature at which the analysis was performed.

(d) Thermostat: An electrically operated thermostatic water bath was used. It was provided with sufficient thermal lagging, suitable heaters and timers with proper cooling arrangements for continuous work. A xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperature accurately, with fluctuations of not more than ±0.1°C. The temperatures were recorded by means of an accurate
sensitive thermometer, reading to tenths of a degree. The bath liquid was water, covered with a layer of liquid paraffin to minimize evaporation of water and loss of heat due to radiation.

**Absorption Cells**

The absorption cells were of quartz and of 4 ml capacity. All the cells were thoroughly cleaned by aqueous ethanol and acetone, and dried before they were used for the spectral measurements. After the transfer of the solution to the cell, care was taken such that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

**Kinetic Measurements**

For all the kinetic determinations, pseudo-first-order reaction conditions have been used, wherein the substrate was taken in large excess over that of the oxidant.

A known amount of the substrate was taken accurately in a 10 ml standard flask, and the volume made up with the requisite quantities of water (in the case of aliphatic aldehydes and dialdehydes), or with 50% aqueous acetic acid (in the case of heterocyclic aldehydes and \( \alpha-\beta \)-unsaturated aldehydes), or with 70% aqueous acetic acid (in the case of long chain aliphatic aldehydes), so as to make the solutions of the required molarity. Quinolinium dichromate (QDC) was accurately weighed out in a 10 ml standard flask, dissolved, and the volume was made up with water (or aqueous acetic acid). Sufficient time was allowed to compensate for any change of heat during dilution. A known volume of sulfuric acid was taken in a 10 ml standard flask, and the
volume made up with water (or aqueous acetic acid) so as to make the solution of required strength. The three solutions thus prepared (substrate, oxidant and acid), were separately thermostated at the required temperature for 1 h, under a nitrogen atmosphere. Equal volumes of the two solutions of oxidant and acid were mixed. A double amount of the substrate solution was then introduced, and the reaction mixture was shaken well. The reaction mixture remained homogeneous throughout the duration of the reaction.

The progress of the reaction was followed by observing the disappearance of Cr(VI). Readings were taken at regular intervals of time, by noting the decrease in absorbance at 440 nm, spectrophotometrically.

All the kinetic experiments were carried out in duplicate or triplicate, and the rate constants which were determined were found to be reproducible to within ±3 %. All reactions were performed under a nitrogen atmosphere. Since the reactions were performed at high concentrations of acid, the ionic strength was not maintained constant.

Calculations

(a) Rate constants

The pseudo-first-order rate constant, \( k_1 \), expressed in s\(^{-1}\), was calculated from the equation (1):

\[
k_1 = \left( \frac{2.303}{t} \right) \log \left( \frac{A_0}{A_t} \right)
\]  

(1)

where \( A_0 \) was the initial absorbance of the reaction mixture, and \( A_t \) was the absorbance at time \( t \). The logarithmic plots of absorbance against time were linear, and extrapolation to zero time gave the value of \( A_0 \).
The values of the second order rate constant, \( k_2 \), expressed in M\(^{-1}\) s\(^{-1}\), were computed by dividing the pseudo-first-order rate constant \( (k_1, \text{s}^{-1}) \) by the concentration of the substrate (M).

(b) Thermodynamic activation parameters

The activation parameters were determined from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows:

(i) Activation energy \((E)\)

From the linear plot of \( \log k_1 \) against the reciprocal of temperature \((T)\),

\[
\text{Slope} = - \frac{E}{2.303R}
\]

\[
E = - \text{slope} \times 2.303R \quad \text{(kJ mol\(^{-1}\))}
\]

(ii) Enthalpy of activation \((\Delta H^* )\)

\[
\Delta H^* = E - RT \quad \text{(kJ mol\(^{-1}\))}
\]

(iii) Entropy of activation \((\Delta S^* )\)

\[
k_1 = \frac{kT}{h} \times e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}}
\]

\[
\Delta S^* = 2.303R \left[ \log k_1 + \frac{\Delta H^*}{2.303RT} - \log kT / h \right] \quad \text{(JK\(^{-1}\) mol\(^{-1}\))}
\]

where \( k \) is the Boltzmann constant, \( h \) is the Planck's constant, and \( R \) is the gas constant.

(iv) Free energy of activation \((\Delta G^* )\)

\[
\Delta G^* = \Delta H^* - T\Delta S^* \quad \text{(kJ mol\(^{-1}\))}
\]
Stoichiometry

The stoichiometric experiments were carried out under nitrogen, at the particular temperature under the conditions of \([\text{QDC}]_0 > [\text{Substrate}]_0\) at varying acid concentrations. The disappearance of Cr(VI) was followed, until the absorbance values became constant. The \([\text{QDC}]_\infty\) was estimated. For each oxidation reaction, the stoichiometric ratio, \(\Delta[\text{QDC}] / \Delta[\text{Substrate}]\), was obtained. The individual stoichiometric equations have been shown along with the reactions of each of the substrates with the oxidant.

Test for Radical formation

Various tests were performed to determine whether radical intermediates were formed during the course of the oxidation reactions of the substrates by quinolinium dichromate (QDC), in acid medium, under nitrogen. The following tests were carried out:

(a) Reduction of mercuric chloride (2):

It was observed that there was no reduction of mercuric chloride, thus indicating the absence of radical intermediates during the process of oxidation of the substrates by QDC.

(b) Polymerization of an added olefinic monomer, such as acrylonitrile (2):

1 ml of acrylonitrile (0.02 M) and 2 ml of substrate solution (0.2 M) in water (in the case of aliphatic aldehydes and dialdehydes), or with 50% aqueous acetic acid (in
the case of heterocyclic aldehydes and $\alpha$-$\beta$-unsaturated aldehydes), or with 70% aqueous acetic acid (in the case of long chain aliphatic aldehydes) and $\text{H}_2\text{SO}_4$ (4.0 M), were taken in a 10 ml conical flask. In a separate test tube, 2 ml of QDC solution (0.02 M) was taken. The two reactant solutions were placed under nitrogen, and then mixed and allowed to stand at 40°C for 30 minutes. There was no formation of a white opalescence, indicating the absence of any polymer formation. The reaction mixture was warmed to 60°C in order to accelerate the oxidation. There was no formation of polymer. Each experiment was accompanied by a blank control.

**Product Analysis**

**(A-i) General Procedure for the oxidation of Aliphatic Aldehydes by QDC.**

Water (30 ml) was taken and cooled in ice. Concentrated $\text{H}_2\text{SO}_4$ (8 ml, 0.15 M) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 9.52 g, 0.02 M) was added, and the mixture was warmed to 40°C for complete dissolution of the QDC. To this mixture, 0.015 M of substrate (0.661 g acetaldehyde, 0.871 g propionaldehyde, 1.082 g butyraldehyde, 1.29 g valeraldehyde, 1.29 g isovaleraldehyde, 1.082 g isobutyraldehyde, 0.871 g glyoxal and 1.5 g glutaraldehyde), taken in 25 ml of water, was added. The reaction mixture was stirred at 40°C for 1 h. The colour changed from yellow to green. The organic layer was extracted with ether (4 x 25 ml), and the combined organic extracts were washed with water, dried (anhydrous $\text{Na}_2\text{SO}_4$), and warmed to remove the ether. The oxidized products [acetic acid (from acetaldehyde);
propionic acid (from propionaldehyde); butyric acid (from butyraldehyde); valeric acid (from valeraldehyde); isovaleric acid (from isovaleraldehyde); iso-butyric acid (from isobutyraldehyde); oxalic acid (from glyoxal); and glutaric acid (from glutaraldehyde)] were obtained after the complete removal of ether (yield ≈ 80-90%). Each reaction product obtained was subjected to IR (KBr) and NMR (300 MHz; CDCl$_3$; Me$_4$Si) analysis, and characterized as follows:

(i) Acetic acid ; IR : \( \nu \) 2945(br s, -OH), 2663, 1711(s, C=O), 1405, 1350, 1291, 940, 620 cm$^{-1}$

1$^1$H NMR : \( \delta \) 11.1 (s, 1H, 1-H), 2.3 (s, 3H, 2-H$_3$)

(ii) Propionic acid ; IR : \( \nu \) 2980(br s, -OH), 2540, 1714(s, C=O), 1467, 1234, 1079, 930, 841 cm$^{-1}$

1$^1$H NMR : \( \delta \) 10.2 (s, 1H, 1-H), 2.4 (q, 2H, 2-H$_2$), 1.1 (t, 3H, 3-H$_3$)

(iii) Butyric acid ; IR : \( \nu \) 2972(br s, -OH), 1716(s, C=O), 1420, 1236, 1105, 937, 762, 490 cm$^{-1}$

1$^1$H NMR : \( \delta \) 10.3 (s, 1H, 1-H), 2.3 (t, 2H, 2-H$_2$), 1.7 (m, 2H, 3-H$_2$), 0.9 (t, 3H, 4-H$_3$)

(iv) Valeric acid ; IR : \( \nu \) 2940(br s, -OH), 2630, 1720(s, C=O), 1427, 1220, 940, 750 cm$^{-1}$

1$^1$H NMR : \( \delta \) 11.2 (s, 1H, 1-H), 2.3 (t, 2H, 2-H$_2$), 1.6 (m, 2H, 3-H$_2$), 1.2 (m, 2H, 4-H$_2$), 0.9 (t, 3H, 5-H$_3$)

(v) Isovaleric acid ; IR : \( \nu \) 2940(br s, -OH), 2623, 1703(s, C=O), 1470, 1301, 1225, 940, 780 cm$^{-1}$

1$^1$H NMR : \( \delta \) 11.1 (s, 1H), 2.2 (m, 3H), 1.0 (d, 6H)
(vi) Isobutyric acid; IR: v 2972(br s, -OH), 2650, 1712(s, C=O), 1465, 1280, 1080, 930, 830 cm⁻¹

\[ ^1H \text{ NMR: } \delta \quad 11(\text{ s, 1H}), 2.6(\text{m, 1H}), 1.2(\text{d, 6H}) \]

(vii) Oxalic acid; IR: v 3425(br s, -OH), 1718(s, C=O), 1685, 1406, 1262, 910, 725, 600 cm⁻¹

\[ ^1H \text{ NMR: } \delta \quad 9.9(\text{ br s, 2H}) \]

(viii) Glutaric acid; IR: v 2707(br s, -OH), 1696(s, C=O), 1467, 1305, 1265, 1085, 920, 761 cm⁻¹

\[ ^1H \text{ NMR: } \delta \quad 11.4(\text{ br s, 2H, 1-H}), 2.3(\text{t, 4H, 2-H}_2), 1.6(\text{m, 2H, 3-H}_2) \]

(A-ii) **General Procedure for the oxidation of long chain Aliphatic Aldehydes by QDC.**

Water (30 ml) was taken and cooled in ice. Concentrated H₂SO₄ (7.9 g, 0.08 M) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolinium dichromate (QDC 9.52 g, 0.02 M) was added and the mixture was warmed to 40°C for complete dissolution of the QDC. To this mixture, 0.015 M of substrate (1.502 g of caproaldehyde, 1.712 g of heptaldehyde, 1.92 g of caprylaldehyde, 2.134 g of pelargonaldehyde, 2.344 g of caprinaldehyde) taken in 25 ml of 70% aqueous acetic acid, was added. The reaction mixture was stirred at 40°C for 24h under nitrogen. The organic layer was extracted four times with ether (25 ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na₂SO₄. The oxidized products (caproic acid (from
caproaldehyde); heptanoic acid (from heptaldehyde); caprylic acid (from caprylicaldehyde); pelargonic acid (from pelargonaldehyde); and capric acid (from caprinaldehyde)] were obtained after the complete removal of ether (yields \( \approx 85-90\% \)). Each reaction product obtained was subjected to IR (CHCl\(_3\)) and NMR (300 MHz; CDCl\(_3\); Me\(_4\)Si) analysis, and characterized as follows:

(i) Caproic acid; IR: \( \nu 2940(\text{br s, -OH}), 2635, 1703(\text{s, C=O}), 1455, 1280, 1210, 930, 731 \text{ cm}^{-1} \)
1\text{H} NMR: \( \delta 10.6(\text{s, 1H, 1-H}), 2.5(\text{t, 2H, 2-H}2), 1.2(\text{m, 6H, 3,4,5-H}2), 0.9(\text{t, 3H, 6-H}3) \)

(ii) Heptanoic acid; IR: \( \nu 2930(\text{br s, -OH}), 2650, 1710(\text{s, C=O}), 1465, 1370, 1285, 1225, 930, 721 \text{ cm}^{-1} \)
1\text{H} NMR: \( \delta 11.1(\text{s, 1H, 1-H}), 2.3(\text{t, 2H, 2-H}2), 1.1-1.3(\text{m, 8H, 3,4,5,6-H}2), 0.9(\text{t, 3H, 7-H}3) \)

(iii) Caprylic acid; IR: \( \nu 2950(\text{br s, -OH}), 2680, 1700(\text{s, C=O}), 1465, 1380, 1295, 1215, 1115, 940, 730 \text{ cm}^{-1} \)
1\text{H} NMR: \( \delta 10.9(\text{s, 1H, 1-H}), 2.4(\text{t, 2H, 2-H}2), 1.2-1.4(\text{m, 10H, 3,4,5,6,7-H}2), 0.9(\text{t, 3H, 8-H}3) \)

(iv) Pelargonic acid; IR: \( \nu 2940(\text{br s, -OH}), 2630, 1720(\text{s, C=O}), 1475, 1370, 1280, 1240, 940, 735 \text{ cm}^{-1} \)
1\text{H} NMR: \( \delta 10.2(\text{s, 1H, 1-H}), 2.3(\text{t, 2H, 2-H}2), 1.4-1.6(\text{m, 12H, 3,4,5,6,7,8-H}2), 0.9(\text{t, 3H, 9-H}3) \)
(v) Capric acid; IR: \( \nu \) 2945 (br s, -OH), 2710, 1700 (s, C=O), 1470, 1300, 1220, 1190, 1080, 940, 740 cm\(^{-1}\)

\(^{1}\text{H NMR: } \delta \)

11.5 (s, 1H, 1-H), 2.3 (t, 2H, 2-H\(_2\)), 1.3-1.6 (m, 14H, 3,4,5,6,7,8,9-H\(_2\)), 0.9 (t, 3H, 10-H\(_3\))

(B) General Procedure for the oxidation of Heterocyclic Aldehydes by QDC

Water (30 ml) was taken in a round bottom flask and cooled in ice. Concentrated H\(_2\)SO\(_4\) (7.9 g, 0.08 M) was added slowly, with constant cooling. When the acid solution had cooled to room temperature, quinolininium dichromate (QDC 9.52 g, 0.02 M) was added and the mixture was warmed to 40\(^\circ\)C for complete dissolution of the QDC. To this mixture, 0.015 M of substrate (1.45 g of 2-furaldehyde, 1.43 g of 2-pyrrolecarbaldehyde, 1.69 g of 2-thiophenecarbaldehyde, 1.61 g of 2-pyridinecarbaldehyde and 3-pyridinecarbaldehyde, 1.66 g of 5-methyl-2-furaldehyde and 2.63 g of 5-bromo-2-furaldehyde) taken in 25 ml of 50% aqueous acetic acid solution, was added. The reaction mixture was stirred at 40\(^\circ\)C for 48 h under nitrogen. The organic layer was extracted four times with ether (25 ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na\(_2\)SO\(_4\). The oxidized products [2-furancarboxylic acid (from 2-furaldehyde); 2-pyrrolecarboxylic acid (from 2-pyrrolecarbaldehyde); 2-thiophenecarboxylic acid (from 2-thiophenecarbaldehyde); 5-methyl-2-furancarboxylic acid (from 5-methyl-2-furaldehyde); 5-bromo-2-furancarboxylic acid (from 5-bromo-2-furaldehyde); 2-pyridinecarboxylic acid (from 2-pyridinecarbaldehyde); and 3-pyridinecarboxylic acid (from 3-pyridinecarbaldehyde)] were obtained (yield \( \approx \) 80-90\%) after the complete
removal of ether. Each of the reaction products obtained was subjected to IR (KBr) and
NMR (CDCl₃ ) analysis, and characterized as follows:

(i) 2-Furancarboxylic acid ;

IR : ν 3000, 2860(br s, -OH), 2583, 1690(s, C=O), 1470, 1305,
1245, 1020, 930, 760 cm⁻¹

¹H NMR : δ 10.5(s, 1H, COOH), 7.9(d, 1H, 5-H), 7.3(d, 1H, 3-H),
6.7(t, 1H, 4-H)

(ii) 2-Pyrrolecarboxylic acid ;

IR : ν 3000, 2850(br s, -OH), 1692(s, C=O), 1545, 1355, 1105,
925, 750 cm⁻¹

¹H NMR : δ 10.2(s, 1H, COOH), 6.9(d, 1H, 5-H), 6.7(d, 1H, 3-H),
6.2(t, 1H, 4-H)

(iii) 2-Thiophenecarboxylic acid ;

IR : ν 3090, 2850(br s, -OH), 2621, 1690(s, C=O), 1530, 1350,
1100, 910, 750 cm⁻¹

¹H NMR : δ 11.4(s, 1H, COOH), 7.8(d, 1H, 5-H), 7.5(d, 1H, 3-H),
7.1(t, 1H, 4-H)

(iv) 5-Methyl-2-furancarboxylic acid ;

IR : ν 2865(br s, -OH), 2630, 1645(s, C=O), 1410, 1370, 1210,
1030, 940, 810, 760 cm⁻¹

¹H NMR : δ 10.4(s, 1H, COOH), 7.5(d, 1H, 3-H), 7.3(d, 1H, 4-H),
2.3(s, 3H, CH₃)
(v) 5-Bromo-2-furancarboxylic acid;
   IR: ν 3130, 2565(br s, -OH), 1700(s, C=O), 1470, 1350, 1220,
   1160, 1020, 940, 860, 760 cm\(^{-1}\)
   \(^1\)H NMR: δ 10.3(s, 1H, COOH), 7.5(d, 1H, 3-H), 6.6(d, 1H, 4-H)

(vi) 2-Pyridinecarboxylic acid;
   IR: ν 3030(br s, -OH), 2500, 1720(s, C=O), 1590, 1305, 1255,
   1040, 830, 680 cm\(^{-1}\)
   \(^1\)H NMR: δ 8.9(s, 1H, COOH), 8.2(d, 1H, 6-H), 8.1(d, 1H, 3-H),
   7.7(m, 2H, 4,5-H)

(vii) 3-Pyridinecarboxylic acid;
   IR: ν 3030(br s, -OH), 2445, 1720(s, C=O), 1590, 1300, 1195,
   830, 680 cm\(^{-1}\)
   \(^1\)H NMR: δ 9.1(s, 1H, COOH), 8.8(s, 1H, 2-H), 8.2(d, 1H, 6-H),
   7.5(m, 2H, 4,5-H)
(C) General Procedure for the oxidation of \( \alpha,\beta \)-Unsaturated Aldehydes by QDC

Freshly distilled substrate solutions (0.71g of methacrylaldehyde, 0.57g of acrylaldehyde, 0.71g of crotonaldehyde, and 1.33g of cinnamaldehyde, 0.01 M) and QDC solution (9.52g, 0.02 M) were mixed in the presence of sulfuric acid (7.9g, 0.08 M) in 50% aqueous acetic acid medium at 40°C. The reaction mixture was stirred under a nitrogen atmosphere for 24h for completion of the reaction. The organic layer was extracted four times with ether (25 ml each time), and the combined organic extracts were washed with water and dried over anhydrous Na\(_2\)SO\(_4\). The oxidized products [methacrylic acid (from methacrylaldehyde); acrylic acid (from acrylaldehyde); crotonic acid (from crotonaldehyde); and cinnamic acid (from cinnamaldehyde)], were obtained after the complete removal of ether (boiling and melting points were in agreement with literature values; yield \( \approx \)80-90%). Each reaction product obtained was subjected to IR (CCl\(_3\)) and NMR (300 MHz ; CDCl\(_3\); Me\(_4\)Si) analysis, and characterized as follows:

(i) Methacrylic acid;

IR : \( \nu \) 2940(br s, -OH), 2500, 1700(s, C=O), 1640, 1455, 1381, 1200, 950, 810 cm\(^{-1}\)

\(^1\)H NMR : \( \delta \) 11.6(s, 1H, 1-H), 6.3(d, 1H, trans to COOH), 5.6(d, 1H, cis to COOH), 2.0 ( s, 3H, CH\(_3\))
(ii) Acrylic acid;

IR : v 3000, 2665(br s, -OH), 1710(s, C=O), 1620, 1300, 1240, 1040,
980 cm\(^{-1}\)

\(^1\)H NMR : \(\delta\) 12.1(s, 1H, 1-H), 6.1(t, 1H, 2-H), 5.9(d, 2H, 3-H\(_2\)),

(iii) Crotonic acid;

IR : v 2920(br s, -OH), 2600, 1700(s, C=O), 1650, 1530, 1440, 1381,
1230, 970 cm\(^{-1}\)

\(^1\)H NMR : \(\delta\) 11.9(s,1H, 1-H), 6.7(s, 1H, 3-H), 5.8(s, 1H, 2-H), 2.0(d, 3H, 4-H)

(iv) Cinnamic acid;

IR : v 3060, 2980(br s, -OH), 1680(s, C=O), 1580, 1450, 1330, 1220,
980, 760 cm\(^{-1}\)

\(^1\)H NMR : \(\delta\) 12.9(s, 1H, 1-H), 8.1(d, 1H, 3-H), 7.7(m, 5H,5,6,7,8,9-H), 6.5(d, 1H, 2-H)
REFERENCES
